POLARIZED ABSORPTION SPECTRA OF
SINGLE CRYSTALS OF LUNAR
PYROXENES AND OLIVINES

ROGER G. BURNS, FRANK E. HUGGINS, and RATEB M. ABU-EID

*Department of Earth and Planetary Sciences, Massachusetts Institute of Technology,
Cambridge, Mass., U.S.A.*

Abstract. Measurements have been made of the polarized absorption spectra (360–2200 nm.) of compositionally zoned pyroxene minerals in rocks 10045, 10047 and 10058 and olivines in rocks 10020 and 10022. Specimens in the form of petrographic thin sections were mounted on polarizing microscopes equipped with three-axis universal stage attachments and inserted into a Cary 17 spectrophotometer. The Apollo 11 pyroxenes with relatively high Ti/Fe ratios were chosen initially to investigate the presence of crystal field spectra of Fe^{2+} and Ti^{3+} ions in the minerals.

Broad intense bands at about 1000 and 2100 nm. arise from spin-allowed, polarization-dependent transitions in Fe^{2+} ions in pyroxenes. Several weak sharp peaks occur in the visible region. Peaks at 402, 425, 505, 550 and 585 nm. represent spin-forbidden transitions in Fe^{2+} ions, while broader bands at 460–470 nm. and 650–660 nm. are attributed to Ti^{3+} ions. Charge transfer bands, which in terrestrial pyroxenes often extend into the visible region, are displaced to shorter wavelengths in lunar pyroxenes. This feature correlates with the absence of Fe^{3+} ions in these minerals. The magnitudes of the intensity ratios: band 465 nm. (Ti^{3+}) to band 1000 nm. (Fe^{2+}) are similar to Ti/Fe ratios from lunar pyroxene bulk chemical analyses, suggesting that an appreciable amount of titanium occurs as Ti^{3+} ions in the lunar pyroxenes. The 505 nm. spin-forbidden peak in Fe^{2+}, together with absorption at 465 nm. by Ti^{3+}, contribute to the pink or pale reddish-brown colors of lunar pyroxenes in transmitted lights.

The absorption spectral measurements not only provide information on the redox behavior and crystal chemistry of lunar pyroxenes, but also form a basis for interpreting spectral reflectivity properties of lunar rocks and the Moon's surface.

1. Introduction

It is well known that the presence of transition metal ions in silicates leads to absorption in the visible and nearby infrared and ultraviolet regions of the electromagnetic spectrum (Burns, 1970a). From an absorption spectrum it is possible to identify the oxidation states and coordination symmetries of the major cations in silicate minerals. The relevance of such measurements to lunar studies is demonstrated in this paper, in which polarized absorption spectra of single crystals of pyroxenes and olivines in certain Apollo 11 rocks have been used to characterize the iron and titanium cations and to interpret reflectivity spectral features measured on the Moon's surface.

2. Experimental

Measurements were made in the region 360–2200 nm. on a Cary model 17 ratio recording spectrophotometer modified to hold two polarizing microscopes equipped with universal stage attachments (Burns, 1966). Lunar samples in the form of conventional petrographic thin sections were mounted on either the microscope flat-stage or

the three-axis universal stage and oriented so that the desired crystallographic or indicatrix axis of the mineral was parallel to the plane of polarization of the lower calcite Nicol prism of the microscope. This microscope technique enabled polarized spectral measurements to be made on crystals with diameters as small as 0.5 mm (500 μ). Thus, it was impossible to avoid using compositionally zoned or exsolved mineral phases. In this preliminary study 30 to 40 μ thick sections were used with the result that absorption bands attributed to Ti^{3+} ions in the pyroxenes and the spin-forbidden peaks due to Fe^{2+} ions in the pyroxenes and olivines were rather weak. Another difficulty was encountered in base-line calibration in the region 600–700 nm. in which the detector systems for visible and near infrared radiation overlap but are outside their optimum ranges of sensitivity.

3. Results: Pyroxenes

Measurements were made on pyroxenes from rocks 10045, 10047 and 10058, analyses of which are described elsewhere (Agrell *et al.*, 1970; Brown *et al.*, 1970; Dence *et al.*, 1970; Hollister and Hargraves, 1970; Keil *et al.*, 1970; Lovering and Ware, 1970; Ross *et al.*, 1970). The pyroxenes have significant iron and titanium contents, are compositionally zoned and contain varying proportions of exsolved augite-pigeonite lamellae.

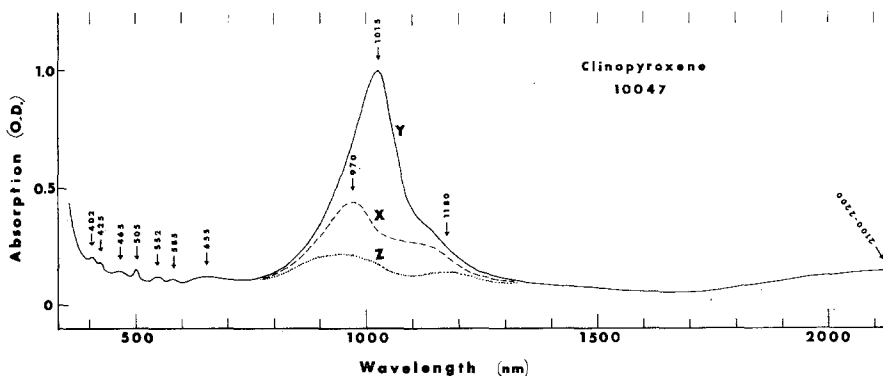The polarized spectra of a typical lunar pyroxene are illustrated in Figure 1 and

Fig. 1.   Polarized absorption spectra of clinopyroxene single crystals in rock 10047.

compared with a terrestrial ferro-augite and pigeonite in Figures 2 and 3. The following features are noteworthy:

(1) The three polarized spectra of each lunar pyroxene crystal are polarization dependent, particularly in the region centered around 1000 nm. The most intense band occurs in the Y spectra (or X spectra of pigeonites) in which light is polarized along the b crystallographic axis of the pyroxene. The relative intensity and absorption maxima of this band at 985–1025 nm. varies from crystal to crystal in each lunar rock.
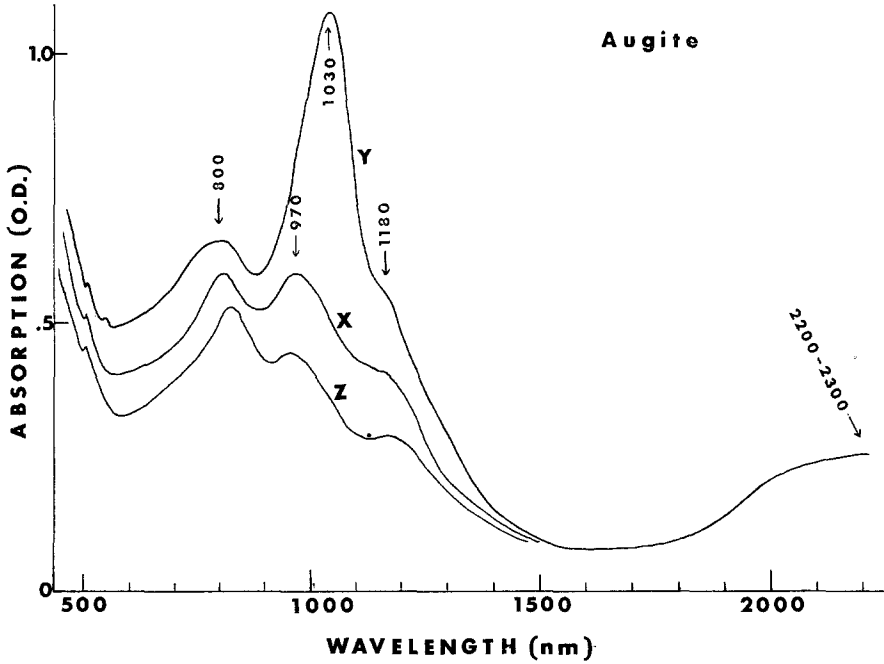
Fig. 2. Polarized absorption spectra of a terrestrial calcic clinopyroxene. The specimen is from a metamorphosed iron formation in Quebec.
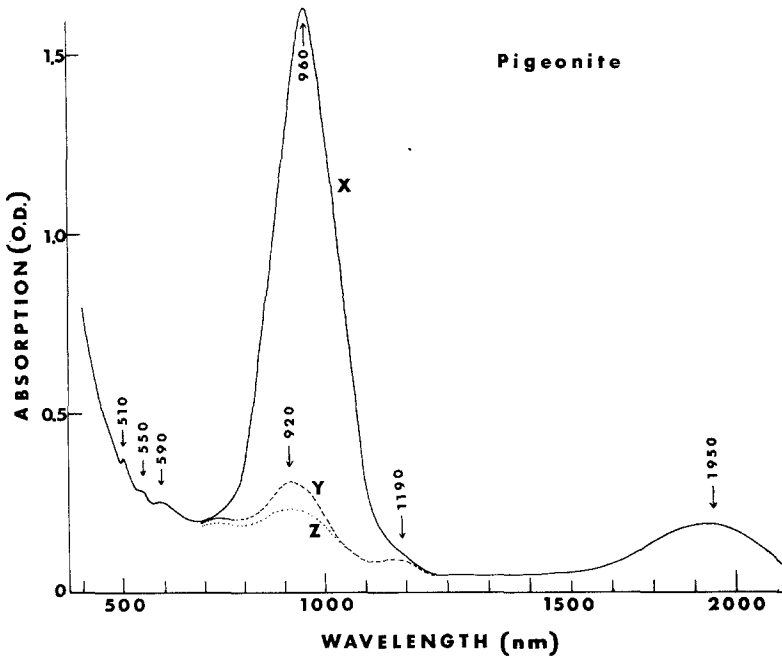

Fig. 3. Polarized absorption spectra of a terrestrial pigeonite. The specimen is from Hakone volcano, Japan.

These features are intermediate between those observed in terrestrial augites and pigeonites, reflecting the compositional variations and differing proportions of exsolved augite and pigeonite in the pyroxenes from Apollo 11 rocks.

(2) A broad band occurs in the region around 2000 nm. The large width of this band compared to terrestrial augites and pigeonites, together with its intermediate position, again correlates with the observed zoning and exsolution features in the lunar pyroxenes.

(3) In contrast to many terrestrial chain silicates such as augites, no intense absorption band occurs in the region 700–800 nm. This band has been assigned to charge transfer between adjacent Fe^{2+} and Fe^{3+} ions in the pyroxene structure (Faye et al., 1968; Burns, 1970a). Its absence in lunar pyroxenes correlates with the virtual absence of Fe^{3+} ions as determined by chemical analysis and Mossbauer spectroscopy of the lunar minerals (Frondel et al., 1970; Hafner and Virgo, 1970; Gay et al., 1970).

(4) The absorption edge representing oxygen-metal charge transfer is located below 360 nm. in lunar pyroxenes, whereas in terrestrial pyroxenes it frequently extends well into the visible region. This distinction may again be attributed to the absence of Fe^{3+} ions in the lunar pyroxenes.

(5) Numerous weak, sharp and broad absorption peaks occur in the visible region. This is shown in more detail in Figure 4. As discussed later, the sharp peaks at 402, 425, 505, 550 and 585 nm. are attributed to spin-forbidden transitions in Fe^{2+} ions, while spin-allowed transitions in Ti^{3+} ions account for the broader bands centered around 465 and 660 nm. (compare figure 6).

INTERPRETATION.

The Fe^{2+} ion, with the electronic configuration $[A]\, 3d^6$, gives rise to the $^5T_{2g}$ quintet
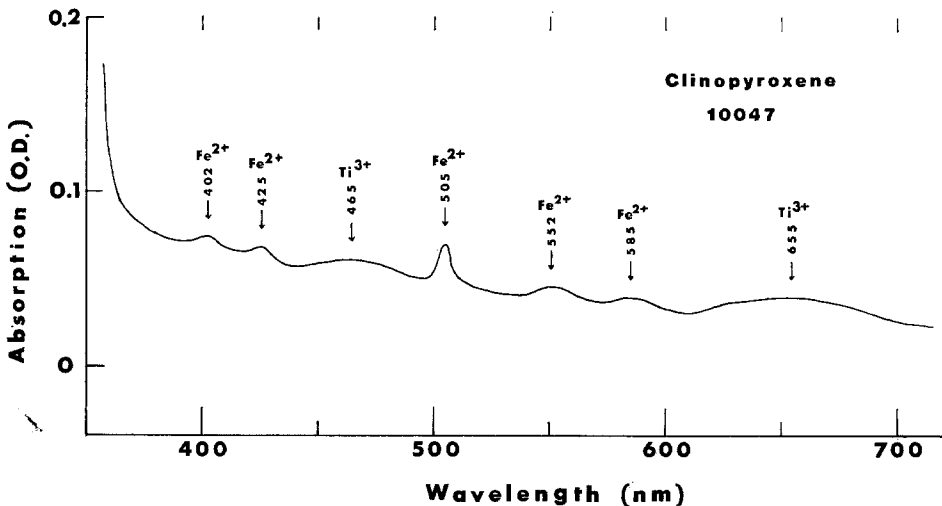

Fig. 4.   Absorption spectrum of a lunar clinopyroxene crystal from rock 10047 in the visible region. Peak maxima and band assignments are indicated.

crystal-field ground-state in octahedral coordination, corresponding to a d electron configuration $(t_{2g})^4 (e_g)^2$ with four unpaired electrons (Burns, 1970a). Numerous excited states are possible (Figure 5), but only one, the ^5E_g state corresponding to the $(t_{2g})^3 (e_g)^3$ configuration, has four unpaired electrons. The remainder are triplet or singlet states corresponding to electronic configurations with two or zero unpaired electrons, respectively. Therefore, in octahedral coordination only one spin-allowed transition, $^5T_{2g} \rightarrow {}^5E_g$, is allowed by group theory selection rules, and this usually
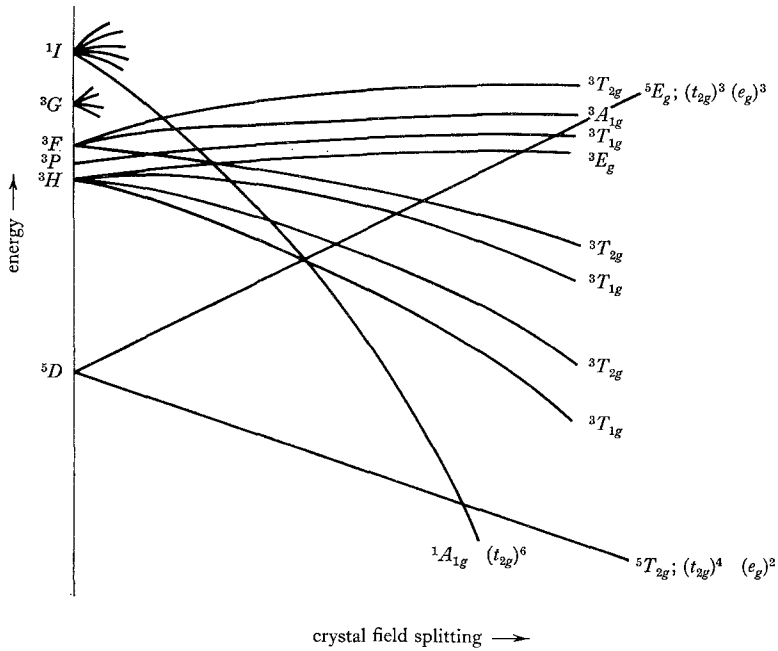

Fig. 5. Energy level diagram for the Fe^{2+} ion in an octahedral crystal field.

leads to absorption in Fe^{2+} ions around 1000 nm. in oxide structures. However, in the pyroxene structure the oxygen coordination polyhedra about the cations are distorted from octahedral symmetry so that the energy levels of the triply degenerate $^5T_{2g}$ and doubly degenerate ^5E_g states are further resolved and additional spin-allowed transitions are possible which are polarization dependent (Bancroft and Burns, 1967; White and Keester, 1967). Such transitions produce the intense broad bands centered around 1000 and 2000 nm. in pyroxenes.

Although transitions from the quintet $^5T_{2g}$ ground-state to the triplet excited states are spin-forbidden, the selection rules are relaxed somewhat by spin-orbit coupling, i.e., the interaction of magnetic moments induced by electrons spinning about their centers of mass and rotating in orbitals around the nucleus. In general, spin-forbidden transitions rarely exceed one-tenth the intensity of spin-allowed transitions in the same cation. Thus, in terms of the energy level diagram for Fe^{2+} shown in Figure 5, the

sharp peaks at 585, 550, 505, 425 and 402 nm. probably represent transitions to the low-lying triplet states of Fe^{2+}.

The Ti^{3+} ion, with the $[A]\,3d^1$ configuration gives rise to a $^2T_{2g}$ ground-state $(t_{2g})^1\,(e_g)^0$ and ^2E_g excited state $(t_{2g})^0\,(e_g)^1$ in octahedral coordination. One spin-allowed transition only is expected in Ti^{3+} ions located in a regular octahedral site, but no spin-forbidden transitions are possible. However, by analogy with Fe^{2+}, distorted octahedral sites in the pyroxene structure are expected to lead to additional absorption bands in the polarized spectra of Ti^{3+}. Thus, the broad bands observed at about 465 nm. and 660 nm. are interpreted as spin-allowed transitions to the resolved components of the ^2E_g excited state of Ti^{3+} ions. The low intensities of these Ti^{3+} bands relative to those in Fe^{2+} ions around 1000 and 2000 nm. are indicative of low Ti/Fe ratios; which in the relatively titaniferous clinopyroxenes of the Apollo 11 rocks rarely exceed 0.1. In terrestrial titanaugites with higher Ti/Fe ratios, the absorption bands attributed to Ti^{3+} ions (Chesnokov, 1959; Burns et al., 1964; Manning and Nickel, 1969) are intensified, particularly around 460 nm. This is demonstrated by the spectrum shown in Figure 6, which not only contains the spin-allowed transitions in Ti^{3+} ions, but also shows the spin-allowed and some spin-forbidden transitions in Fe^{2+}, together with the $Fe^{2+} - Fe^{3+}$ charge transfer band located on the shoulders of the oxygen-metal charge transfer band extending well into the visible region.

An alternative interpretation of the weak peaks in the visible and ultra-violet regions of lunar pyroxenes has been suggested invoking Fe^{3+} ions (Cohen, 1970,
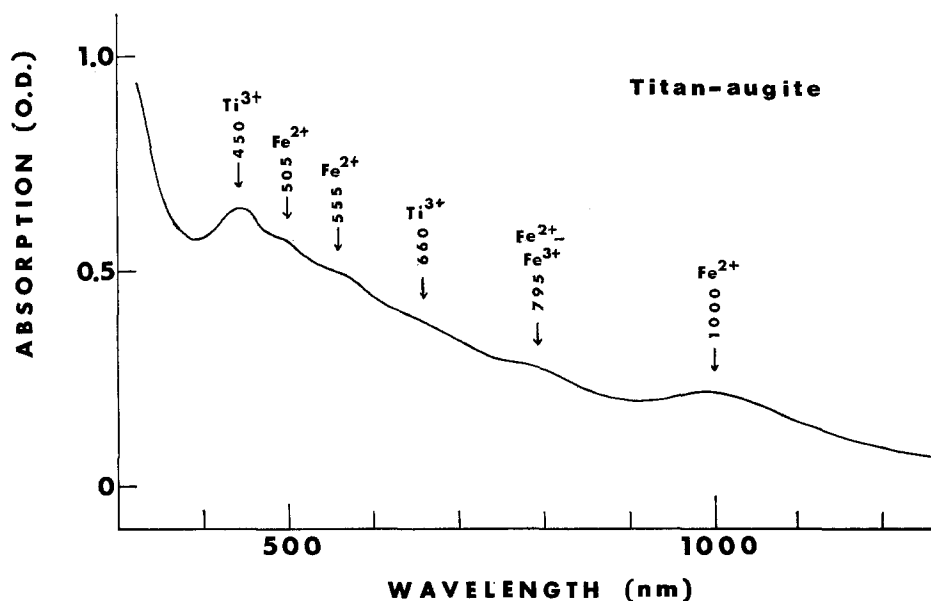

Fig. 6.   Absorption spectrum of a terrestrial titanaugite.
The specimen is from Mt. Unimas in the Caroline Islands.

1971). This interpretation is rejected for the following reasons. Since *all d* electron transitions in high-spin Fe^{3+} ions are spin-forbidden, the ferric ion concentration in lunar pyroxenes must be comparable to the Fe^{2+} ion contents in order to account for the intensities of the peaks attributed to Fe^{3+} ions. This postulate is at variance with other evidence cited earlier pointing to negligible Fe^{3+} ions in the lunar pyroxenes.

4. Results: Olivines

Measurements were made on olivines in rocks 10020 and 10022, analyses of which have been published (Agrell *et al.*, 1970; Dence *et al.*, 1970; Keil *et al.*, 1970; Haggerty *et al.*, 1970; Kushiro and Nakamura, 1970; Weill *et al.*, 1970). In general, compositional zoning in the lunar olivines is not as pronounced as it is in the pyroxene phases and no exsolution features have been found in the olivines. The polarized absorption spectra of a typical lunar olivine, which are remarkably similar to terrestrial olivines (Burns,
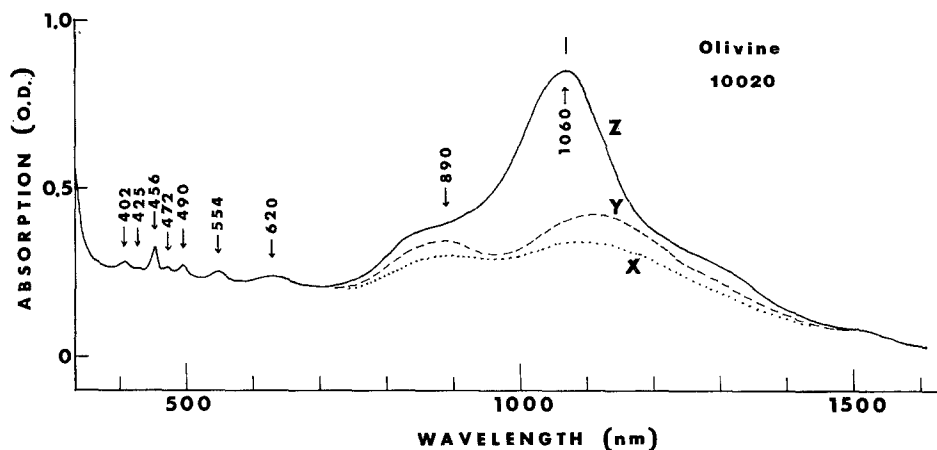
Fig. 7.   Polarized absorption spectra of olivine single crystals in rock 10020.

1970b), are shown in Figure 7. By analogy with the spectra of lunar pyroxenes in Figures 1 and 4, there are several noteworthy features shown in the olivine spectra:

(1) The broad bands occurring around 1000 nm. are attributed to spin-allowed transitions in Fe^{2+} ions. These bands display the diagnostic polarization dependence (or pleochroism) found in terrestrial olivines (Burns, 1970a, b) with the most intense band occurring in the Z polarized spectra (*a* crystallographic axis) around 1055–1065 nm. The position of this band varies from crystal to crystal correlating with the compositional zoning measured in lunar olivines. The zoning is also demonstrated in Figure 8, which shows that the lunar olivines conform to the linear peak maxima-composition trends established for terrestrial olivines (Burns, 1970b).

(2) Numerous sharp peaks are located in the visible region of lunar olivines which are again attributed to spin-forbidden transitions in Fe^{2+} ions.

(3) The absorption edge representing metal-oxygen charge transfer transitions is located well into the ultraviolet region, in contrast to terrestrial olivines where absorption extends into the visible region. This feature again correlates with the negligible contents of Fe^{3+} ions in lunar olivines, although the Fe^{3+} ion contents of terrestrial olivines are also generally low.
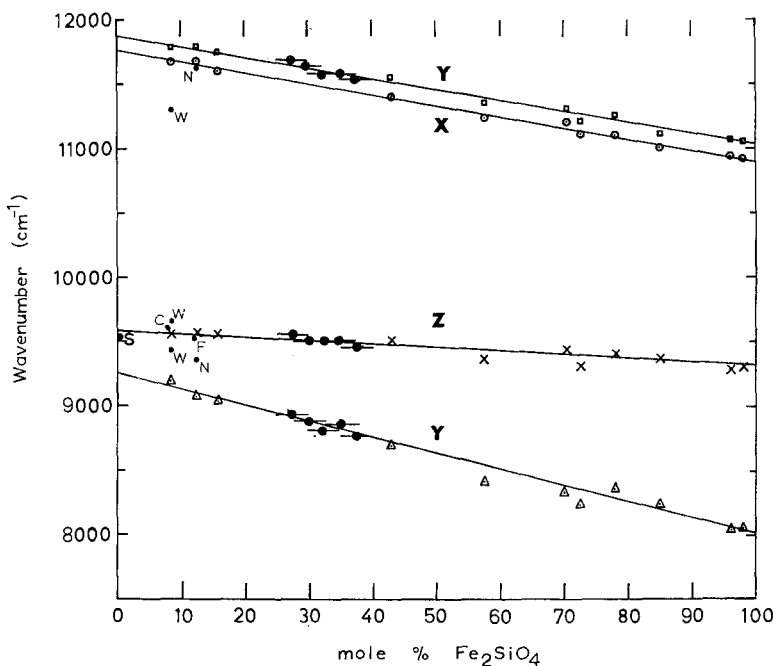

Fig. 8. Compositional variations of the peak maxima in the polarized absorption spectra of Mg-Fe olivines. —●— olivines from rocks 10020 and 10022.

One other feature in the lunar olivine spectra measured in this study is the absence of evidence for Cr^{2+} ions suggested by Haggerty *et al.* (1970). They observed one weak, poorly observed band superimposed on the polarized Fe^{2+} spectra at about 1040 nm., and another weak band occurring as a shoulder centered at about 720 nm. We question these findings on the grounds that the low Cr/Fe ratio, about 1/140, in their lunar olivine specimen would make it virtually impossible to resolve spectral features due to the low abundance of Cr^{2+} ions. Clearly, further work is required, particularly on the more chromian olivines in the Apollo 12 rocks.

5. Discussion of Results

The absorption spectral data further demonstrate the complex crystal chemistry of pyroxenes from the Apollo 11 rocks. The peak maxima correlate with the observed finely exsolved augite-pigeonite lamellae and with the measured compositional zoning

in the lunar pyroxenes. With the identification of Ti^{3+} ions in the lunar pyroxenes by absorption spectroscopy, it will be necessary to re-interpret the crystal chemistry and chemical trends of pyroxenes from the Apollo 11 rocks (Burns, in preparation). This is caused by the earlier assumption that all titanium occurs in the Ti(IV) oxidation state in these minerals (Ross *et al.*, 1970; Hollister and Hargraves, 1970; Bence *et al.*, 1970). The presence of Ti^{3+} ions in lunar pyroxenes provides further evidence of the low oxygen fugacities that must have existed during the cooling history of the Moon (Agrell *et al.*, 1970; Bailey *et al.*, 1970; Brown *et al.*, 1970; O'Hara *et al.*, 1970).

Certain physical properties of lunar materials may be explained by the absorption spectra. For example, the 505 nm. spin-forbidden peak in Fe^{2+}, together with the absorption at 465 nm. by Ti^{3+} ions, contribute to the pink or pale reddish-brown colors of lunar pyroxenes in transmitted light. These peaks also contribute to the spectral features around 500 nm. observed in reflectance measurements of lunar materials and from telescopic observations of the Moon's surface (Adams and Jones, 1970; Adams and McCord, 1970, 1971; Conel and Nash, 1970). Our measurements demonstrate that spin-forbidden transitions in Fe^{2+} ions produce peaks having intensities comparable to the Ti^{3+} bands. Furthermore, the pronounced band centered around 950 nm. in reflectance spectra of the Moon's surface has components originating from the spin-allowed transitions in Fe^{2+} ions occurring in octahedral coordination in pyroxenes and olivines.

Acknowledgments

References

Note: the 3-volume publication: 'Proceedings of the Apollo 11 Lunar Science Conference', *Geochimica Acta,* Vol. **34**, is abbreviated to: *Proc. Apollo 11 Conf.*

Adams, J. B. and Jones, R. L.: 1970, *Science* **167**, 737–739.
Adams, J. B. and McCord, T. B.: 1970, *Proc. Apollo 11 Conf.* **3**, 1937–1945.
Adams, J. B. and McCord, T. B.: 1971, *Proc. 2nd Lunar Sci. Conf.* **3**, 2183.
Agrell, S. O., Scoon, J. H., Muir, I. O., Long, J. V. P., McConnell, J. D., and Peckett, A.: 1970, *Proc. Apollo 11 Conf.* **1**, 93–128.
Bailey, J. C., Champness, P. E., Dunham, A. C., Esson, J., Fyfe, W. S., Stumpfl, E. F., and Zussman, J.: 1970, *Proc. Apollo 11 Conf.* **1**, 169–174.
Bancroft, G. M. and Burns, R. G.: 1967, *Am. Mineral.* **52**, 1278–1287.
Bence, A. E., Papike, J. J., and Prewitt, C. T.: 1970, *Earth Planetary Sci. Letters* **8**, 393–399.
Brown, G. M., Emeleus, C. H., Holland, J. G., and Phillips, R.: 1970, *Proc. Apollo 11 Conf.* **1**, 195–219.
Burns, R. G.: 1966, *J. Sci. Intr.* **43**, 58–60.
Burns, R. G.: 1970a, *Mineralogical Applications of Crystal Field Theory,* Cambridge Univ. Press.
Burns, R. G.: 1970b, *Am. Mineral.* **55**, 1608–1632.
Burns, R. G., Clark, R. H., and Fyfe, W. S.: 1964, *Proc. Vernadsky Cent. Symp.* **2**, 88–106 (transl. Israel Progr. Sci. Transl).
Chesnokov, B. V.: 1959, *Dokl. Acad. Sci.* **129**, 1162–1164.
Cohen, A. J.: 1970, *Trans. Am. Geophys. Union* **52**, 272.

Cohen, A. J.: 1971, *Proc. Conf. Lunar Geophys.* (Abstract).

Conel, J. E. and Nash, D. B.: 1970, *Proc. Apollo 11 Conf.* **3**, 2013–2023.

Dence, M. R., Douglas, J. A. V., Plant, A. G., and Traill, R. J.: 1970, *Proc. Apollo 11 Conf.* **1**, 315-340.

Faye, G. H., Manning, P. G., and Nickel, E. H.: 1968, *Am. Mineral* **53**, 1174–1201.

Frondel, C., Klein Jr., C., Ito, J., and Drake, J. C.: 1970, *Proc. Apollo 11 Conf.* **1**, 445–474.

Gay, P., Bancroft, G. M., and Bown, M. G.: 1970, *Proc. Apollo 11 Conf.* **1**, 481–498.

Hafner, S. S. and Virgo, D.: 1970, *Proc. Apollo 11 Conf.* **3**, 2183–2198.

Haggerty, S. E., Boyd, F. R., Bell, P. M., Finger, L. W., and Bryan, W. B.: 1970, *Proc. Apollo 11 Conf.* **1**, 513–538.

Hollister, L. S. and Hargraves, R. B.: 1970, *Proc. Apollo 11 Conf.* **1**, 541–550.

Keil, K., Bunch, T. E., and Prinz, M.: 1970, *Proc. Apollo 11 Conf.* **1**, 561–598.

Kushiro, I. and Nakamura, Y.: 1970, *Proc. Apollo 11 Conf.* **1**, 607–626.

Lovering, J. F. and Ware, N. G.: 1970, *Proc. Apollo 11 Conf.* **1**, 633–654.

Manning, P. G. and Nickel, E. H.: 1969, *Canad. Mineral.* **10**, 71–83.

O'Hara, M. J., Biggar, G. M., Richardson, S. W., Ford, C. E., and Jamieson, B. G.: 1970, *Proc. Apollo 11 Conf.* **1**, 695–710.

Ross, M., Bence, A. E., Dwornik, E. J., Clark, J. R., and Papike, J. J.: 1970, *Proc. Apollo 11 Conf.* **1**, 839–848.

Weill, D. F., McCallum, I. S., Bottinga, Y., Drake, M. J., and McKay, G. A.: 1970, *Proc. Apollo 11 Conf.* **1**, 937–955.

White, W. B. and Keester, K. L.: 1967, *Am. Mineral.* **52**, 1508–1514.